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UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

COLLEGE OF ARTS & SCIENCE
DEPARTMENT OF CHEMISTRY
BROWN CHEMICAL LABORATORY
PHONE: 302-738-2461

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"COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS"

Professor Harold C. Bescheil

Principal Investigator

September, 1968

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Dr. B. T. Wolfson (SREP)
1400 Wilson Boulevard
Arlington, Virginia 22209

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i. FOREWORD

This research at the University of Delaware under Grant AF-AFOSR 922-67 for the period May 1, 1968 through July 31, 1968 was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force.

ii. ABSTRACT

Combustile tubes, loaded with sample powders, have demonstrated their utility in screening pure and catalyzed monopropellant oxidizer burning rates. Tests have been run at pressures from 1 to 100 atmospheres; and various perchlorates and nitrates have been tested.

Divalent cation doping of A.P. large single crystals has proven to be extremely difficult. Tests are proceeding with Ba^{++} . Concurrent tests in other laboratories have demonstrated burning rate modification of propellants containing divalent ion doped, granular A.P.

DTA tests have shown that both tetraphenylthiophene and its precursor tetraphenylcyclopentadienone have the high stability useful for combustion modification.

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I. Introduction

A fundamental understanding of the combustion characteristics of a range of physical conditions of crystalline oxidizers is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research involves theoretical and experimental studies of the burning of crystalline oxidizers ranging in physical form from large single crystals to low bulk density powders. A strandburner, window bomb and high-speed motion picture photography will be used to obtain burning rates versus pressure, and to record stability of combustion for a variety of particle sizes and pressure (density) packings of selected crystalline oxidizers (i.e., ammonium perchlorate) and analogous compounds. The study of large single crystal burning will remove particle size, shape, and packing factors as complications. Data from low bulk density powder combustion studies, when compared with single crystal data, provides vital information about the characteristic surface, combustion zone thickness, ignition and conductivity contributions to the overall combustion phenomena.

In addition, it is believed that simple combustion tests of powder oxidizer samples can serve as an efficient screening technique for determining whether chemical modifications have increased or decreased the intrinsic burning rate. Crystalline decomposition mechanisms observed during burning will be related to the oxidizer intrinsic burning rate and the basic properties of the oxidizer such as chemical nature, crystal type, and ion sizes. The validity of the models will be determined by correlation with the experimental data obtained.

II. Pure Oxidizer Combustion

Ambient pressure and temperature burning rates of substituted ammonium perchlorates have been determined and reported in quarterly No. 3 (February through April, 1968);⁽¹⁾ for methylammonium perchlorate (MAP), dimethyl ammonium perchlorate (DMAP) and trimethyl ammonium perchlorate (TMAP) and compared with pure ammonium perchlorate (AP). These rates were for powder samples burned in insulating combustible tubes. The powders were loaded into the sample holding tubes and

packed to 50% of crystal density. The particle size was held at -40 + 50 mesh, and the materials were stored at room temperature and 5% RH before testing. All of these oxidizers were tested in sample tubes ranging from 4 mm. to 10 mm. in diameter.

These tests have shown that a variety of pure crystalline oxidizers will burn reproducibly under ambient laboratory conditions in combustible sample tubes having an i.d. of 6.5 mm.

Where burning is steady and reproducible, the diameter does not greatly affect the burning rate. For some oxidizers, tubes as small as 4 mm. i.d. will suffice. For others, burning will always quench shortly after the ignition source is removed when using that small diameter. For still other oxidizers, a reproducible type of pulsating or unstable combustion takes place in tubes as large as 6 mm. i.d. However, when the diameter is increased to 6.5 mm. i.d., this pulsation ceases. When tubes are made 8 mm. i.d. and larger, we find that the combustion surface departs widely from planar, and coning develops.

To summarize:

- a. The AP always burned reproducibly in 6 mm. tubes and most of the time in 4 mm. tubes. In 8 mm. and larger tubes, unburned oxidizer remained behind the more rapid flame front passing down the periphery to give a coning effect.
- b. The MAP quenched in 4 mm. tubes, but burned reproducibly in 6 mm. and larger tubes.
- c. The DMAP quenched in 4 mm. tubes, pulsated in 6 mm. tubes and burned reproducibly in 6.5 mm. and larger tubes.
- d. The TMAP quenched in 4 mm., but burned reproducibly in 6 mm. and larger tubes.

When we originally made the selection of waxed paper tubes (common soda straws) as sample holders for combustion tests, we did so to:

- a) minimize heat loss to the surroundings

- b) minimize heat conduction down the sample tube to the unburnt portions, and
- c) to prevent undesirable fluid dynamic effects through having the exhaust gases confined to a jet when passing up through an unconsumed tube.

We fully realized that the fuel value of the burning tube might present some complications, but decided to accept that undesirable feature as opposed to acceptance of the heating and flow effects in a), b), c) above; such as by using a glass or metal tube. We found that most oxidizers tested would give measurable and reproducible burning rates under ambient conditions; whereas, this is not true with uninsulated metal or glass.

At this point we have demonstrated the utility of 4.0 to 6.5 mm. diameter cylindrical soda straws, loaded with candidate oxidizers in readily available granular form, as a screening test technique for demonstrating monopropellant burning rate changes - as small compositional changes are made in the oxidizer. These changes in rate were explained by thermochemical and kinetic factors.

The combustion of a variety of pure oxidizers at elevated pressures in glass sample tubes was capably reported by von Elbe and McHale(2).

III. Attempted Doping of Ammonium Perchlorate Single Crystals

All attempts to date to substitute Sr^{++} for NH_4^+ in large single crystals of AP have been unsuccessful. Apparently, the differences in ion size caused the difficulty. NH_4^+ has a radius of 1.48 \AA vs. a Sr^{++} radius of 1.10 \AA . Although we have attempted the substitution of Sr^{++} into the AP lattice using very slow crystallization, and over a wide variety of concentration ranges, we have never been able to find a detectable level of Sr^{++} in perfect AP crystals. We were mislead several times into thinking that we had introduced Sr^{++} into large single crystals only to find that, by careful inspection of the crystals to eliminate all flaws, and careful washing of the crystal surfaces, we could no longer find any Sr^{++} present. Fine

crystals of doped AP or co-crystallized AP and SrClO_4 are readily prepared by cooling of a solution of both salts. However, our goal is to insert the Sr^{++} as a replacement ion in the lattice of the large single AP crystals. We had previously grown monovalent cation doped A.P. (Rb^+); and Naval Weapons Center has been growing K^+ doped A.P. crystals(5).

We are now trying to get Ba^{++} doping of AP because its ion size is closest to that of NH_4^+ of all available ions ($\text{Ba}^{++} \approx 1.29\text{A}$ radius). We may have some difficulty because the barium salt is about 15 times more soluble than AP. Strontium was originally chosen because its solubility was near that of AP.

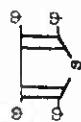
The divalent cations are intended to stabilize the electronic structure of AP according to a theory proposed by J. N. Maycock of RIAS(3,4). Maycock has shown that fine crystalline AP doped with divalent cations has improved thermal stability in DTA, TGA, and isothermal tests. Conversely, he has found that AP doped with divalent anions, in accord with the theory, has lower thermal stability. Further, it was proposed that lowered thermal stability would lead to higher burning rates when the oxidizer was used in propellant - and first tests have shown this to be so.(5)

IV. Combustion Modifiers

We have been surveying compounds available for the modification of burning. Initial attention is being given to organic compounds, that are essentially carbon and hydrogen (to retain ultimate fuel value) and have highly stable structures. We theorize that such compounds would have a good chance of slowing surface decomposition and near surface gas zone kinetics so that burning rates would be reduced. We are looking at tetr phenylthiophene (TPTP) and its precursor, tetra phenylcyclopentadienone.

The differential thermal analysis results for the neat compounds are shown in Figures 1 and 2 respectively. The melting of TPTP is seen as a sharp endotherm at about 182°C . The vaporization is seen as another sharp endotherm at 470°C . There appears to be some impurity in the sample showing up as an endotherm at 133°C . However, it can be seen that there is no exothermic decomposition reaction up to

FIGURE 1. DTA THERMogram TETRAPIENYLTHIOPHENE



SIZE: Micro 3 mm
REF: Glass bead
RATE: 20°C/min
START: 38.9°C

ATM. N₂
SCALE SETTING: 2°C/in.

DuPont Model 900

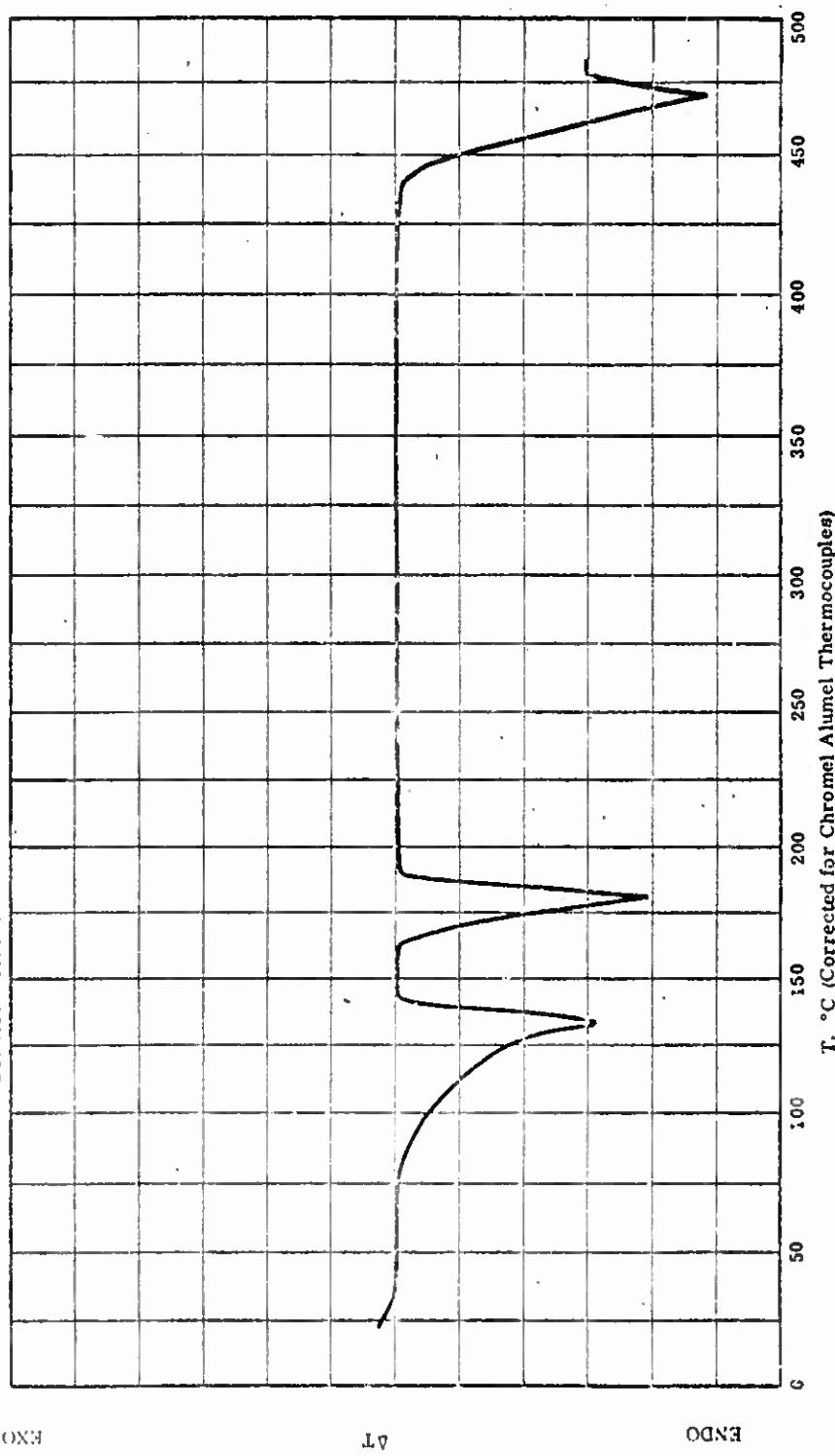


FIGURE 2. DTA THERMOGRAM: TETRAPHENYLCYCLO-PENTADIENONE
(Aldrich Chemical Company)

III

SIZE: Micrc (3 mm)
REF: Glass head
RATE: 20°C/min
START: 39.4°C

ATM.
SCALE SETTING:
N₂ 2°C/in.

DuPont Model 900

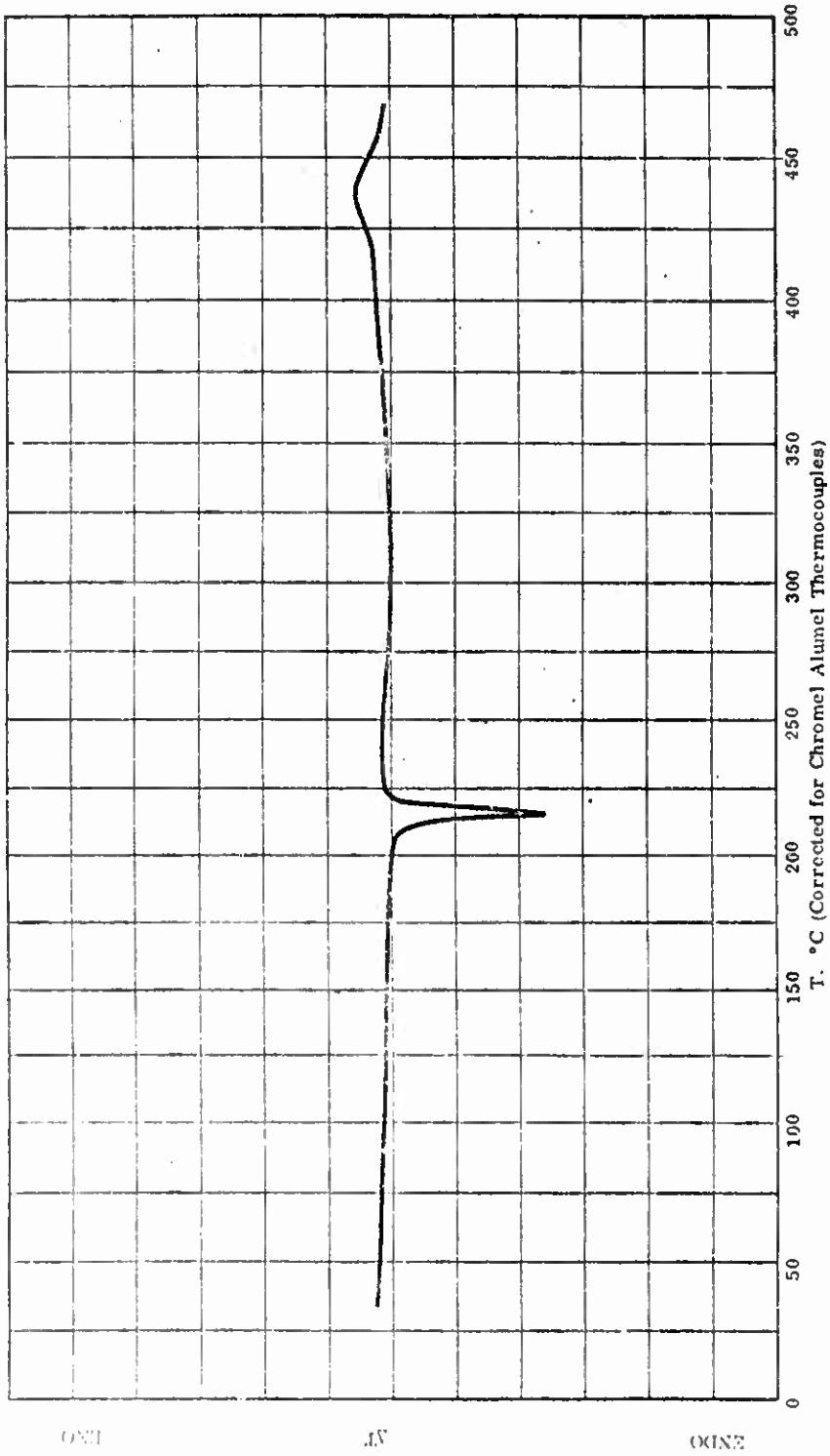


Table 1

STRAND SAMPLE PREPARATION AND COMBUSTION DATA

Sample Number	Composition and Inhibitor	Weight (grams)		Active Length (cm)	Active Vol. cc	Bulk Density g/cc	Burning Rate (in/sec)
		Tare	Total	Active			
1	7% Tetraphenyl	0.4655	1.7496	1.2841	8.9	1.1178	1.1488
2	cyclopentadienone	0.4770	1.6910	1.2140	8.35	1.0488	1.1575
3	93% A.P.	0.4574	1.7040	1.2466	8.6	1.0802	1.1540
4	6 mm. i.d. straw	0.4998	1.7178	1.2380	8.5	1.0676	1.1596
5		0.4598	1.7550	1.2958	9.0	1.1304	1.1463
						$\bar{x}_p = 1.1532$	$\bar{x}_b = 0.0423$
6	11% Tetraphenyl	0.4700	1.7728	1.3028	9.25	1.1618	1.1214
7	cyclopentadienone	0.4679	1.8188	1.3509	9.50	1.1932	1.1322
8	89% A.P.	0.4670	1.7916	1.3246	9.40	1.1806	1.1219
9	6 mm. i.d. straw	0.4575	1.7752	1.3209	9.30	1.1681	1.1306
10		0.4761	1.7802	1.3041	9.15	1.1492	1.1348
						$\bar{x}_p = 1.1282$	$\bar{x}_b = 0.0476$

Note: A.P. was 40 - 50 mesh ultra high purity
 Combustion conditions: 20°C, 21.2 atm, 2000 sec (50,000 in/sec)

about 500°C. Temperatures near this level are anticipated at the exposed solid oxidizer surface in propellant combustion.

This extreme stability has been verified in the ambient burning tests where the TPTP was seen to vaporize apparently undecomposed during burning.

In Figure 2 it can be seen that the dienone melts at about 215°C and is stable up to the region of 400°C. In burning rate tests, (see Table 1) with the dienone at ambient conditions, there was some increase in burning rate when 11% by weight was added to the A.P. When only 7% was added, there was no change. The increase at the higher level was possibly caused by the fuel contribution of an impurity. Tests are now needed at higher pressures to see if the extreme stability of these compounds will alter combustion when the high pressures prevent ready vaporization from the surface. We are looking for significant burning rate retardation when about 5% of a given component is added to AP.

V. Conclusions

- 1) Monopropellant oxidizer powders can be rapidly tested for burning rate in common soda straws.
- 2) Diameters should be 4.0 to 6.5 mm. i.d., and active lengths at least three inches long.
- 3) Divalent cation doped, single AP crystals are extremely difficult to grow. Barium ion doping should be the easiest.
- 4) Tetraphenylthiophene and tetraphenylcyclopentadienone have been identified as potential combustion modifiers.

VI. Future Work

- 1) Continue growth of crystals from Ba^{++} containing AP solutions.
- 2) Conduct burning tests at 300 to 100 atmospheres of A.P. powder/combustion modifier mixtures.

VII. References

- 1) H. C. Beachell, E. E. Hackman and Y. C. Kim "Combustion Characteristics of Crystalline Oxidizers" Quarterly Report No 3, University of Delaware, Brown Chemical Laboratory, May, 1968.
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- 5) E. J. Dibble and W. R. McRride, NWC Quarterly Progress Report, Research in Chemistry NWCTP 4605, April-June, 1968, China Lake, Calif.

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Divalent cation doping of A.P. large single crystals has proven to be extremely difficult. Tests are proceeding with Ba⁺⁺. Concurrent tests in other laboratories have demonstrated burning rate modification of propellants containing devalent ion doped, granular A.P.

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Dimethyl Ammonium Perchlorate						
Trimethyl Ammonium Perchlorate						
Burning Rate						
Quenching Diameters						
Crystal Growth						
Crystal Doping						